

Nano-Engineered Electrochemical Sensors for Monitoring of Toxic Metals in Groundwater

Development Of Novel Square Wave Anodic Stripping Voltammetry Electrodes Using Self Assembled Monolayers On Mesoporous Supports

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Acronyms

ATR	Attenuated Total Reflectance
BET	Brunauer-Emmett-Teller analysis
FT-IR	Fourier Transform Infrared
MPTMS	MercaptoPropylTriMethoxySilane
SAM	Self Assembled Monolayer
SAMMS	Self Assembled Monolayer on a Mesoporous Support
SEM	Scanning Electron Microscopy
SH-FMS	Thiol Functionalized Mesoporous Silica
SWASV	Square Wave Anodic Stripping Voltammetry
SWV	Square Wave Voltammetry
TEM	Transmission Electron Microscopy
TEOS	Tetraethoxysilane
XRD	X-Ray Diffraction

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EXECUTIVE SUMMARY

To remediate groundwater tainted with toxic metal ions such as mercury or lead, it would be advantageous to have ion specific sensors for those ions. This project involved coupling novel sorbent materials known as Self Assembled Monolayers on Mesoporous Supports (SAMMS) with electrolytic probes to allow the detection of mercury, lead, and actinides from aqueous solution using Square Wave Anodic Stripping Voltammetry (SWASV). Electrodes were fabricated using three approaches: embedding the SAMMS in a conductive carbon paste, depositing the SAMMS as a thin film to the face of the electrode, and depositing thin film SAMMS to interdigitated electrodes.

Results are presented which demonstrate that these electrodes are a promising selective detection technology. The selectivity of the SAMMS technology coupled with the rapid collection and detection methods afforded by the SWASV technique represent a clear step forward in the development of devices for rapid, fieldable devices for environmental remediation and testing for adherence to water quality standards. The interdigitated electrodes, while a promising idea, did not achieve the desired level of sensitivity; further work would be necessary to advance this technology to a more promising status. The driver for pursuing the interdigitated electrodes is that capacitance can be measured far more precisely than integrated current (as in the SWASV technique); the barrier to success at this juncture would appear to be insufficient sensitivity of the capacitance of the electrodes to the adsorption of the target analytes. Greater capacity for captured analytes in the regions between the interdigitated spokes may address this limitation.

1.0 OBJECTIVE

This document is our final report for SERDP SEED project (SI-1267), “Nano-Engineered Electrochemical Sensors for Monitoring of Toxic Metals in Groundwater.” The work completed under this project addressed the needs of the Department of Defense’s (DoD) Strategic Environmental Research and Development Program (SERDP), for Statement of Need SEEDSON-02-01. The objective of this project was to establish proof-of-principle for a new class of sensors for monitoring toxic metal ions in groundwater utilizing nanoengineered, highly selective, high surface area sorbent materials.

Our project consisted of three tasks. Firstly, we embedded functionalized mesoporous silica-based sorbent materials in conductive carbon paste, and we applied functionalized mesoporous silica thin films to the faces of electrodes. Secondly, we used the electrodes constructed in the first task to perform square wave anodic stripping voltammetry (SWASV) to demonstrate detection of Pb^{2+} and Hg^{2+} from aqueous solution. Finally, we explored the feasibility of depositing the functionalized mesoporous silica thin films to interdigitated electrodes, to determine whether adsorption of metal ions from solution would create a capacitive signal, thereby providing proof of principle of another class of sensor based on functionalized mesoporous silica sorbents.

2.0 BACKGROUND

The present state-of-the-art for groundwater monitoring relies heavily on withdrawal of water samples for subsequent laboratory analysis. This process is time consuming and operator-intensive. The use of *in situ* sensors would obviate much of the sample manipulation and on-site labor required. However, the current generation of sensors for monitoring metal ion concentrations are fairly simple nonselective devices; the typical suite of sensors measure reducing potential, pH, temperature, water level, and conductivity. These sensors record the general chemical nature of the groundwater, but they are insufficient to determine concentrations of particular classes of metals of interest. Species-selective sensors are needed to detect and quantify concentrations of metal ions in aqueous media. The most promising sensors are based on stripping voltammetry. The technique may be enhanced by preconcentration of the target species, which generally involves mixing a preconcentrating agent with a carbon paste or chemically modifying a conductive polymer. As the preconcentrating agent is depleted or poisoned, however, new surfaces must be exposed to maintain the viability of the electrode.

Preconcentrating voltammetric electrodes have been employed to collect and detect nickel onto dimethylglyoximeⁱ (Baldwin et al. 1986), mercury on a diphenylcarbazide-carbon paste electrodeⁱⁱ (Navratilova 1991), lead on crown ethersⁱⁱⁱ (Prabhu et al. 1989), and uranium on trioctylphosphine oxide^{iv} (Lubert et al. 1982). These techniques all utilize the ligand bearing material in loose association or physical contact with the electrode. We propose covalently bonding the functional material to a solid support before distributing it within the conductive matrix.

Stripping voltammetry enhanced by preconcentration may be summarized as depicted in Figure 1, below.

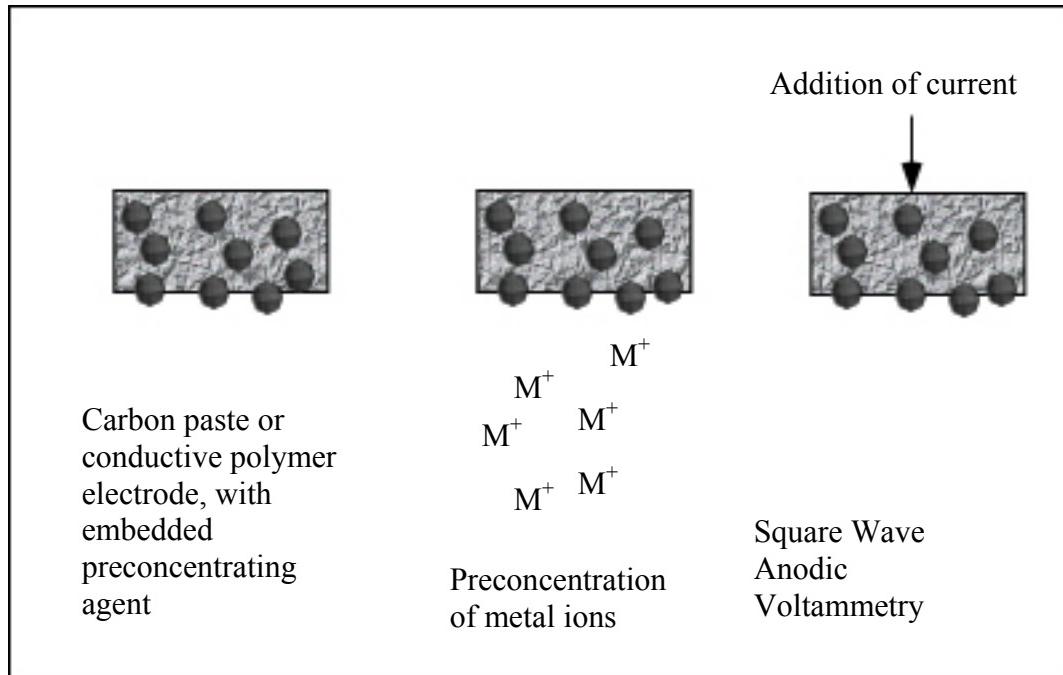


Figure 1: Preconcentration and Square Wave Anodic Stripping Voltammetry

A Self Assembled Monolayer (SAM) is a coating of a single molecule thickness. Consider the idealized illustration shown below in Figure 2a. Three-carbon chains bearing a functional group to anchor to a silica surface on one end and a functional group to fix particular metal ions on the other will arrange themselves into a single monolayer with the metal scavenging end protruding from the surface.

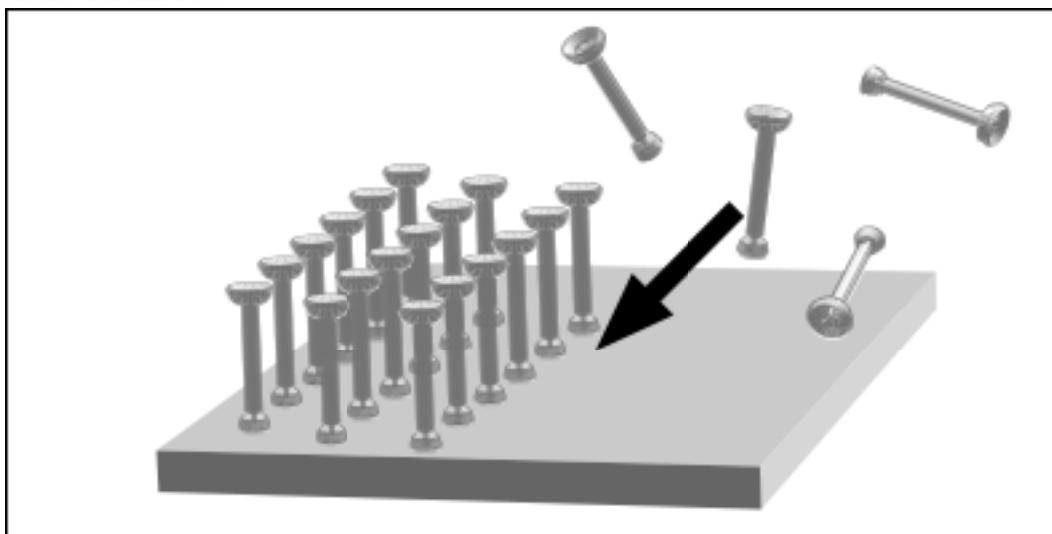


Figure 2a: A Self Assembled Monolayer

Mesoporous silicas are porous materials of extremely high surface area. As substrates for catalytic coatings or sequestration coatings they offer broad applications, from chemical processing to wastewater cleanup^{v,vi} (Kresge et al. 1992; Beck et al. 1992). The mesoporous materials are generated using micellar microemulsions as templates. The surfactant surfaces are chemically modified to produce a solid silicate tubule, which precipitates into an organized lattice and is then thermally crosslinked, calcined, and coated with a self-assembled monolayer to produce the final Self-Assembled Monolayer on Mesoporous Silica (SAMMS). The result is a hexagonal array of regular pores with monodisperse inner diameters, coated with a chemically active species. (See Figure 2b.)

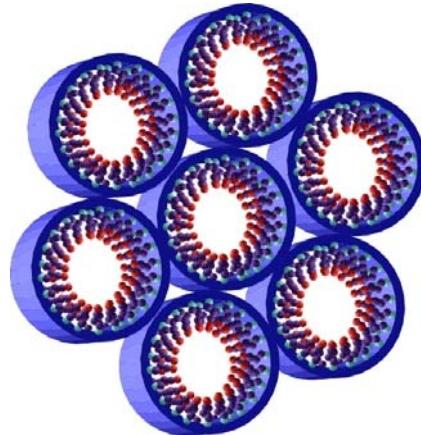


Figure 2b: Multiple Templated Silica Pores with Self Assembled Monolayer

SAMMS are emerging as a new and promising technology, and have been demonstrated to be highly selective sequestration agents for metal ions in aqueous streams.^{vii,viii,ix} (Feng et al. 1997; Liu et al. 1998; Holton 1998) Moreover, the uptake of the targeted metal species from the aqueous medium is remarkably rapid. (See Figure 2c.)

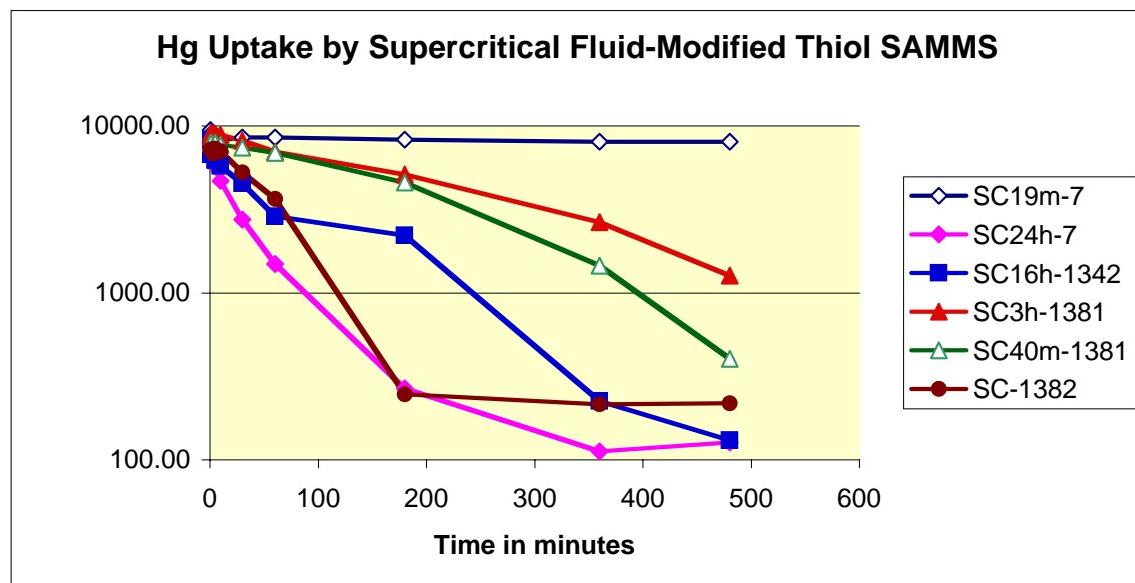


Figure 2c: Hg Uptake

Figure 2c: Hg^{2+} Uptake from Aqueous Solution by Thiol SAMMS. SAMMS were functionalized in Supercritical CO_2 for 19 minutes (SC19m-7), 24 hours (SC24h-7), 16 hours (SC16h-1342), 3 hours (SC3h1381), 40 minutes (SC40m-1381), and 4 hours (SC1382). Three different mesoporous silicas ("batch 7, preparation 1381, and preparation 1382) were used. They differ chiefly in pore size.

Table 1: Distribution Coefficients For Lanthanides On Acetyl Phosphonate SAMMS

<u>Lanthanide</u>	<u>pH=6.5</u>	<u>pH=4.5</u>	<u>pH=2.5</u>	<u>pH=1.0</u>
La	63,233	49,050	1,779	139
Nd	107,300	73,466	4,857	283
Eu	182,100	129,600	14,881	593
Lu	199,800	98,200	488	215

Distribution coefficients (K_d) for the metal ions bound to the SAMMS *vs.* in aqueous solution have been measured as high as 10^8 , and are generally insensitive to pH above $\text{pH} \approx 4$ (See Table 1).

Selection of the ligand headgroup for the SAM allows selective absorption of differing classes of metal ions. For example, a thiol headgroup fixes "soft" heavy metals like mercury, silver, and cadmium. (See Figure 3b.) PNNL is the world leader in development and deposition of functional SAMs on mesoporous silica. The ligands currently under development at PNNL include:

1. thiols (selective for "soft" heavy metals like mercury, cadmium, and silver),
2. amido phosphonates (selective to lanthanides and actinides, and, presumably, alkaline earth metals),
3. salicylamides and phthalamides (broad affinity for transition metals, but over narrow range of pH),
4. glycylurea (similar to the salicylamine SAMMS, but for a wide range of pH and more selective within the actinides), and
5. cationic ethylenediamine complexes (selective to chromate and arsenate).

The selectivity between metal classes allows better characterization of the groundwater chemistry, as well as preserving SAMMS functional surface area. (If several classes of metals are to be targeted, an array of the proposed sensors might be deployed in the same package.)

These characteristics have resulted in advanced technologies for cleanup of arsenic, cadmium, or mercury-tainted streams, as well as for sequestration of actinide species. (This is of obvious importance to the treatment of tank waste streams and groundwater contamination near legacy waste sites.) Removal of mercury from water has been demonstrated, even when the metal ion is present in oxide or organic-complexed form. SAMMS are expected to be similarly aggressive toward oxides and complexes of the other metals of interest as well.

3.0 METHODS

Three methods were employed to construct the electrodes. Firstly, SAMMS were embedded in a conductive carbon paste to create the SWASV electrode. Secondly, a mesoporous silica thin film was deposited to the surface of an electrode and functionalized in the usual fashion. Lastly, a mesoporous silica thin film was deposited on interdigitated electrodes to test whether capacitance change upon metal ion uptake might serve as a useful signal.

3.1 SAMMS in conductive carbon paste

3.1.1 Apparatus

Square wave voltammetry (SWV) experiments were performed on an electrochemical detector, model CHI660A (CH Instruments, Inc.), equipped with a three electrode system: a home-made carbon paste electrode that was modified with SH-SAMMS as the working electrode, a platinum wire as the auxiliary electrode, and a KCl saturated Ag/AgCl electrode as the reference electrode. All measurements were made at room temperature and under an atmospheric environment. Square wave voltammetry was operated at a frequency of 100 Hz with a pulse amplitude of 50 mV and a potential step height of 5 mV.

3.1.2 Working electrodes

The modified carbon paste electrode was prepared by thoroughly mixing 0.05 g of SH-SAMMS with 0.15 g of the CPO carbon paste (Bioanalytical Systems, Inc.). The preparation and characterization of SH-SAMMS with 82% thiol coverage are described elsewhere^x (Chen et al. 1999). A 0.05 g aliquot of mineral oil (Aldrich Co.) was added to the carbon paste mixture and mixed until obtaining a uniformly wetted paste. The final composition (by weight) was 20% SH-SAMMS, 60% CPO carbon paste, and 20% mineral oil. The composition was varied in the electrode composition study. Unmodified carbon paste, prepared in the same fashion but without adding SH-SAMMS, was packed into an 8-cm long PTFE cylindrical tube (geometric area 0.08 cm²) with a copper piston providing an inner electrical contact. Chemically modified carbon paste was packed into the end of the same tube. The electrode surface was smoothed on a weighing paper. When necessary, a new surface was obtained by removing about 2-3 mm (from the surface) of electrode material, adding fresh-made material, and polishing it.

A similar electrode was constructed using SAMMS bearing a carbamoylphosphonic acid ligand headgroup (“Ac-Phos), shown in Figure 3, below. This electrode was used to detect Cd²⁺, Cu²⁺, and Pb²⁺ simultaneously using the SWASV method.

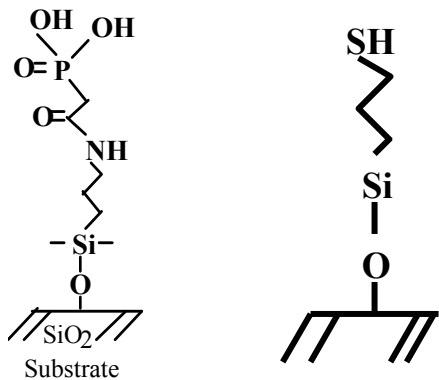


Figure 3: (a) The Ac-Phos self assembled monolayer and (b) the Thiol self assembled monolayer

3.1.3 Voltammetric detection procedure

SAMMS modified carbon paste electrodes contain two components: a nonconductive component (e.g., SAMMS) for adsorption of target metal ions and a conductive component (e.g., carbon graphite) for electrochemical detection. The procedure for measuring metal ion concentrations consisted of preconcentration (e.g., metal ions adsorption on nanopore surfaces inside the SAMMS particles), desorption and cathodic electrolysis (e.g., metal ions release from the nanopore surfaces, diffuse out of the nanopores, and deposit on the surface of graphite particles), detection, and regeneration (if necessary). Table 2 summarizes operating conditions for voltammetric detection experiments. During preconcentration, the electrode was immersed (at 2 cm from the solution surface) in a 20-mL cell (i.d. 2 cm) containing 15 mL of metal ion solution at an open circuit for a specified period of time. Lead (Pb^{2+}) solution and $\text{Pb}^{2+}/\text{Hg}^{2+}$ mixture solution were prepared daily by diluting atomic absorption (AA) standard solutions from Aldrich Co. (comprised of 1000 mg/L of each metal ion in a 1% HNO_3 solution) with ultrapure Millipore water ($18 \text{ M}\Omega\text{-cm}$). The pH of the diluted metal ion solution was between 5 and 6, thus no addition of buffer solution was required. During preconcentration, the solution was efficiently stirred (above 300 rpm). The electrode was removed at the end of the preconcentration step, rinsed with DI water, and transferred to another 20-mL cell containing 15 mL of supporting electrolyte solution (i.e., HNO_3 , KNO_3). A negative potential was applied to the electrode immediately after immersing it into the electrolyte solution, thereby reducing the desorbed metal ion into elemental metal (cathodic electrolysis). The electrolysis step was performed for 60 seconds, except in the electrolysis time study. Stripping voltammetry was subsequently performed by sweeping a square wave potential towards the positive direction (i.e., from -1.0 V to 0.4 V for Pb, from -1.0 V to 0.6 V for Pb/Hg). Quiescent conditions (no stirring) were required in both cathodic electrolysis and stripping steps. The sweeping of a square wave potential toward positive values was performed one more time to ensure that no metal ion was accumulated on the electrode surface. If the surface was clean, no peak would be detected in the second sweep. If a peak is detected, regeneration of the electrode is required for the subsequent run by applying a positive potential (0.4 V for Pb and 0.6 V for Hg/Pb) to the electrode, while the electrode was immersed in 0.2 M HNO_3 under stirred conditions. Unless specified otherwise, each measurement was performed in triplicate and the average value was reported. The relative standard deviations (% RSD) were normally less than 5%. No de-aeration of the samples or solutions was required in any step.

Table 2: Typical operating parameters during each step of the voltammetric detection experiments

Parameter Preconce	ntration	Electrolysis Stripping		Regeneration
Solution/Electrolyte	0.15 – 1500 ppb Pb ²⁺ , 3 – 1600 ppb Hg ²⁺ ,	0.2 M HNO ₃	0.2 M HNO ₃	0.2 M HNO ₃
Immersion time	2 – 20 min	0 – 2 min	—	1 – 2 min
Stirring speed	400 rpm	0	0	400 rpm
Applied potential: Pb	open circuit	-1.0 V	-1 V – 0.4 V	0.4 V
Applied potential: Pb/Hg	open circuit	-1.0 V	-1 V – 0.6 V	0.6 V

3.2 Electrodes coated with a mesoporous thin film

3.2.1 Chemicals and solutions

The non-ionic surfactant used in preparing the SiO₂ film was Pluronic F-127 (EO₁₀₆PO₇₀EO₁₀₆), obtained from BASF Corp. All solutions were of highest purity available, including ethyl alcohol (Gold Shield Chemical Co.), 2-propanol (Aldrich Co.), nitric acid (Aldrich Co.), tetraethyl orthosilicate (TEOS, Aldrich Co.), and 3-mercaptopropyl trimethoxysilane (MPTMS, United Chemical Technologies, Inc.).

3.2.2 Preparation of a SH-FMS thin film modified gold microelectrode array

The modification of a gold electrode array on microchip with a thiol Functionalized Mesoporous Silica (SH-FMS) thin film consisted of two steps. First a mesoporous silica film was deposited onto the electrode surface by the spin-coating technique. Then the thiol functional groups were immobilized inside the mesopores of the film by self-assembly chemistry. To prepare the silica film solution, a 2.578 g quantity of Pluronic F-127 surfactant was dissolved in 3.430 g of de-ionized water and 8.846 g of ethyl alcohol. Then 0.108 g of concentrated HNO₃ was added into the mixture. Finally, a 5.0 g quantity of TEOS was added to the solution. The molar ratio of TEOS: water: ethanol: HNO₃: Pluronic F-127 was 1:8:8:0.05:0.008. The solution was shaken for 24 hours, then spin-coated at the speed of 3000 rpm onto the bare surface of a gold microelectrode array on microchip (part No. M1450110, Microsensor System, Inc.) for 30 seconds. Figure 4a shows the schematic of the microelectrode array. The specific electrode array had 50 finger pairs (15 microns finger width and finger spacing) with gold as the electrode material and quartz as the substrate. The electrical connection for the array was covered with plastic tape before spin coating with the film solution. After the spin coating, the tape was removed and the film-coated electrode was calcined on a hot plate at 350 °C for 8 minutes in air. Following the calcination, immobilization of the thiol groups onto the silica thin film was performed. The film-coated electrode was placed in a 100% humidity chamber at room temperature for 2 hours, and then soaked in 400 mL of toluene at 75°C under a nitrogen atmosphere. A 24 mL volume of MPTMS was added to the resultant electrode, placed within a 1000 mL reflux chamber, and refluxed at 110°C for 5 hours. Finally, the modified electrode was rinsed with copious 2-propanol and dried by blowing with N₂ gas. The final product was an electrode array modified with SH-FMS thin film. Figure 4b depicts the electrode, which is composed of three layers: SiO₂/Au/SH-FMS.

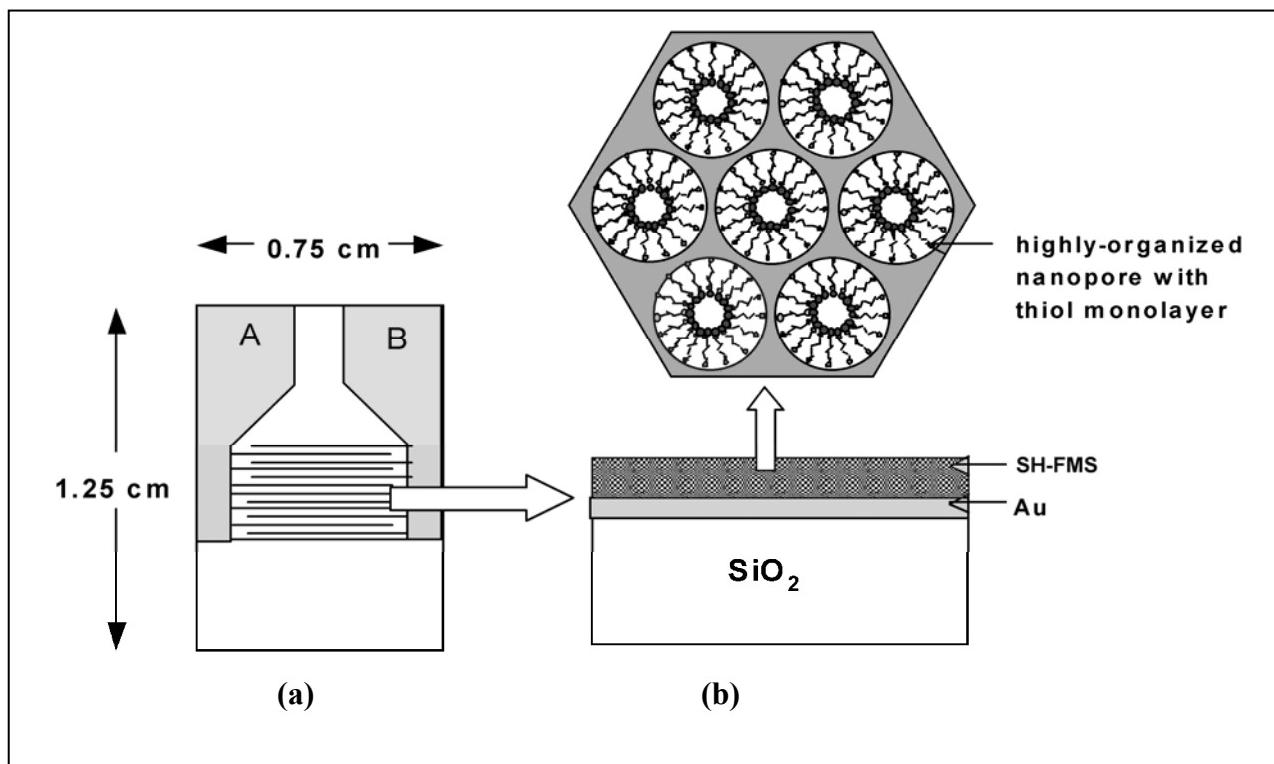


Figure 4: (a) electrode construction (b) compositional cross-section

3.2.3 Characterization of mesoporous silica thin film and SH-FMS thin film

Characterization of the untreated mesoporous silica film and the thiol-treated silica (SH-FMS) thin film was performed using N_2 gas adsorption/desorption (BET), scanning electron microscopy (SEM), XRD, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), an optical profilometer, and ellipsometry.

BET and TEM measurements were performed on untreated film that was detached from the substrate before the analyses. High-resolution TEM analysis was carried out on a JEOL JEM 2010F microscope operating at 200 kV with a specified point-to-point resolution of 0.194 nm. BET surface area, porosity, and pore size analyses were performed on a Quantachrome Autosorb 6-B gas sorption system. The thickness of the untreated film was measured using the Zygo optical profilometer (OMP-0347). Both untreated and functionalized films were analyzed using ellipsometry and FT-IR measurements. The FTIR characterization of the films was performed on a Nicolet MAGNA-IR 860 spectrometer equipped with an attenuated total reflectance (ATR) detector and a MCT-A detector.

3.2.4 Voltammetry measurement procedure

The voltammetric detection of lead (II) with the SH-FMS thin film modified gold electrode was investigated. The voltammetric procedure consisted of preconcentration, cathodic electrolysis, anodic stripping, and regeneration steps. Square wave voltammetry (SWV) experiments were performed on an electrochemical analyzer, model CHI660A (CH Instruments, Inc.), equipped with a three electrode system: a gold microelectrode array on microchip that was modified with a

SH-FMS thin film as the working electrode, a platinum wire as the auxiliary electrode, and a KCl saturated Ag/AgCl electrode as the reference electrode. During the square wave voltammetry experiments, both sides of the electrode array were connected at points A and B (Figure 4a) and used as the working electrode. All measurements were made in an ambient environment. Square wave voltammetry was operated with a frequency of 100 Hz, pulse amplitude of 50 mV, and potential step height of 5 mV. During preconcentration, the electrode was immersed (at 1 cm from the solution surface) in a 20-mL cell (i.d. 2 cm) containing 15 mL of metal ion solution under an open circuit for a specified period of time. Lead (Pb^{2+}) solution was prepared daily by diluting atomic absorption (AA) standard solution (comprised of 1000 mg/L of Pb^{2+} in a 1% HNO_3 solution) from Aldrich Co. with high purity water (18 M Ω -cm). The pH of the diluted metal ion solution was between 5 and 6. During preconcentration, the solution was stirred at over 300 rpm. The electrode was removed at the end of the preconcentration step, rinsed with DI water, and transferred to another 20-mL cell containing 15 mL of supporting electrolyte solution (e.g. 0.1 M HNO_3). During the cathodic electrolysis, a negative potential was applied to the electrode immediately after immersing it into electrolyte solution for a 60-second period (unless specified otherwise) to reduce the desorbed metal ion into elemental metal. Anodic stripping voltammetry was subsequently performed by sweeping a square wave potential toward positive values (i.e. from -0.8 V to 0.3 V). Quiescent conditions (no stirring) were used in both the cathodic electrolysis and stripping steps. No de-aeration of solutions was required in any step. The sweeping of a square wave potential toward positive values was performed one more time to insure that lead was completely removed from the electrode surface. Normally, when the electrolysis and stripping steps were performed in 0.1-0.2 M HNO_3 , no regeneration of the electrode was required (no peak was detected after the re-sweep). Unless specified otherwise, each measurement was performed in duplicate and the average value was reported. The relative standard deviations (% RSD) were normally less than 5%.

3.3 Interdigitated electrodes

The side investigation into whether capacitance could be used as an alternative to SWASV was performed using the thin film-modified electrode described in section 2.2.2. These measurements demonstrated that the technique indeed could work for detection of the presence of the target metal ion in solution, but the sensitivity was quite low. With work, the technique might be refined into a useful device.

4.0 RESULTS

Only the results for Thiol-SAMMS in a carbon paste electrode will be discussed here. The evaluation of a SH-SAMMS modified carbon paste electrode as a voltammetric sensor for metal ions involves optimizing the experimental parameters that affect both the preconcentration and detection steps. Lead (Pb^{2+}) was used as a representative analyte in finding the optimal parameters, which would then be used in subsequent experiments to obtain calibration curves and detection limits for simultaneous detection of Pb^{2+} and Hg^{2+} . Unmodified carbon paste electrodes were shown to be ineffective for uptake and therefore detection of lead.

As noted above, the results for the interdigitated electrodes were inconclusive; this approach has promise, but no conclusive results were obtained to be reported as results of this work.

4.1 Factors affecting the detection process

4.1.1 Electrolysis and stripping media

Because SH-SAMMS is an electronic insulator, desorption of Pb²⁺ previously accumulated on SH-SAMMS to the electrode/solution interface must occur for the voltammetric detection to be possible. Then the desorbed Pb²⁺ may be detected directly by reduction from lead ion to elemental lead (Pb²⁺ → Pb(0)). However, it is more sensitive and quantitative if a thorough electrolysis by applying a negative potential to deposit Pb(0) on the electrode surface, followed by anodic stripping voltammetry to oxidize the previously reduced Pb(0) to Pb²⁺, is performed^{xi} (Etienne et al. 2001).

Different electrolysis and stripping media were investigated with an electrode composed of (by weight) 11% SH-SAMMS, 66% CPO carbon paste, and 23% oil. The experiments were performed at conditions as follows: 100 ppb Pb²⁺ preconcentration solution, 2 minutes preconcentration time, and 60 seconds electrolysis time. The results are summarized in Table 3. Decreased adsorption or increased desorption of Pb²⁺ from SH-SAMMS occurs at low pH⁷ (Feng et al 1997). Therefore, electrolysis and stripping in neutral solution such as 0.1 M KNO₃ was ineffective for detection of lead, leading to no voltammetric response (zero current). When the stripping was performed in acid solutions (0.1 M or 0.2 M HNO₃) after the electrolysis was performed in 0.1 M KNO₃ solution, the voltammetric response (current) increased. However, the most effective lead detection was accomplished by performing both electrolysis and stripping in acid solution. Increasing the concentration of nitric acid solution as the electrolysis and stripping media from 0.05 M to 0.2 M did not significantly improve the sensitivity or reproducibility of lead detection but did decrease the need for regeneration of the electrode for the subsequent run and thus reduced the total analysis time. Therefore, 0.2 M HNO₃ is recommended as electrolysis and stripping media.

Table 3: The effect of electrolysis and stripping media on lead detection

Electrolysis medium	Stripping medium	Current (μA)	% RSD
0.1 M KNO ₃	0.1 M KNO ₃	0	0
0.1 M KNO ₃	0.1 M HNO ₃	1.07	1.3
0.1 M KNO ₃	0.2 M HNO ₃	2.32	2.4
0.05 M HNO ₃	0.05 M HNO ₃	4.15	1.7
0.1 M HNO ₃	0.1 M HNO ₃	3.62	2.9
0.2 M HNO ₃	0.2 M HNO ₃	4.33	1.3

4.1.2 Electrolysis Time

A complete desorption and electrolysis is required for an accurate quantification of lead ions. Figure 5 shows the effect of electrolysis time on the voltammetric response for Pb²⁺ using an electrode composed of (by weight) 10% SH-SAMMS, 60% CPO carbon paste, and 30% oil. The experiments were performed under conditions as follows: 100 ppb Pb²⁺ preconcentration solution, 2 minutes preconcentration time, and 0.2 M HNO₃ as the electrolysis and stripping media. The peak current increased significantly as the electrolysis time was increased from 0 to 60 seconds and remained constant from 60 to 120 seconds. However, the reproducibility of the

data was poor at the 120-second electrolysis period. This is probably due to the generation of H₂ bubbles on electrode surface that affected the stability of the signals. Therefore, a 60-second electrolysis period was chosen for lead deposition. A maximum voltammetric response obtained after an electrolysis period of only 1 minute suggested a rapid desorption and diffusion rate of lead ions from inside the nanopores of SH-SAMMS to the electrode/solution interface.

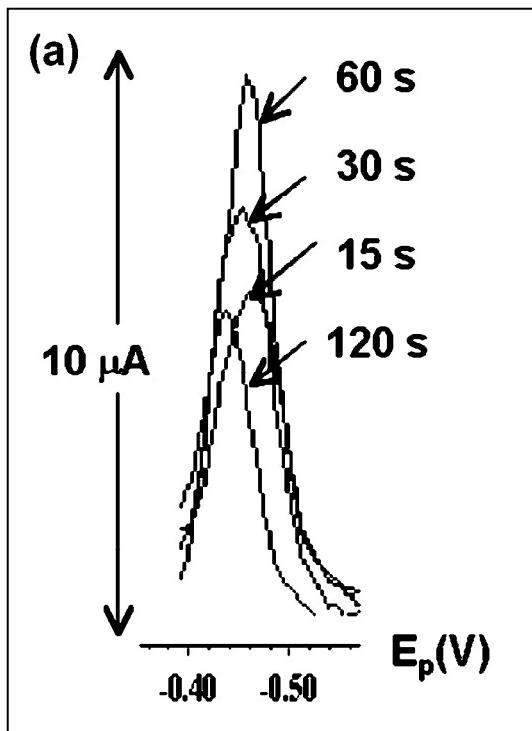


Figure 5: Voltammetric response for Pb²⁺ for varying electrolysis times

4.2 Factors affecting preconcentration process

4.2.1 Preconcentration Time

The effect of preconcentration time on the voltammetric response for Pb²⁺ using an electrode, composed of (by weight) 10% SH-SAMMS, 60% CPO carbon paste, and 30% oil, is shown in Figure 6. The experiments were performed under conditions as follows: 100 ppb Pb²⁺ preconcentration solution, 60 seconds electrolysis time, and 0.2 M HNO₃ as electrolysis and stripping media. Both peak currents and areas increased significantly and in parallel to each other as the preconcentration time was increased from 1 to 20 minutes with a more gradual increase from 20 to 30 minutes. For rapid detection of lead, a 2-minute preconcentration period was found to be sufficient at this concentration range (100 ppb Pb²⁺). For the detection of Pb²⁺ at a much lower concentration (i.e., 1 ppb Pb²⁺), a 20-minute preconcentration period may be required to obtain higher lead adsorption and hence larger peak size.

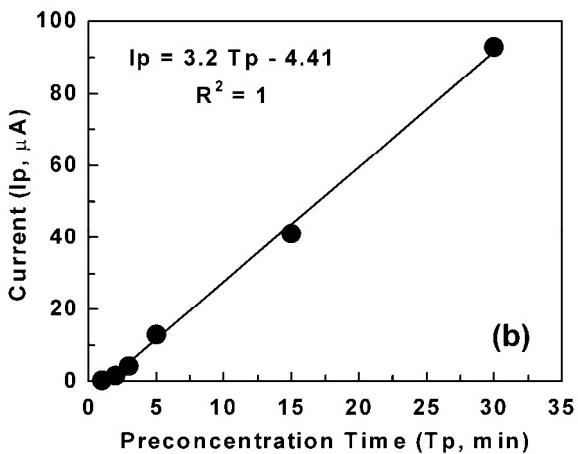


Figure 6: Voltammetric response for Pb^{2+} as a function of preconcentration time

4.2.2 Electrode compositions

Five compositions of the SH-SAMMS modified electrode were studied and the results are summarized in Table 4. The experiments were performed under conditions as follows: 100 ppb Pb^{2+} preconcentration solution, 2 minutes preconcentration time, 60 seconds electrolysis time, and 0.2 M HNO_3 as electrolysis and stripping media. The same experiment was also performed on an unmodified carbon paste electrode. The powdered SH-SAMMS, when used as the modifier in a carbon paste electrode, clearly enhanced the sensitivity of the electrode for lead(II) detection. The experiments performed on the unmodified carbon paste electrode (electrode #1) did not yield any voltammetric responses (currents) for lead, indicating that the conductive matrix (carbon graphite) was inert with respect to lead adsorption, similar to the results found by Walcarius and Bessière.^{xii} (Walcarius and Bessière 1999)

Table 4: The effect of electrode compositions (by weight) on lead detection

Electrode	% SH-SAMMS	% CPO Carbon paste	% Oil	Current (mA)	% RSD
1	0	70	30	0.00	0.0
2	10	60	30	1.29	2.2
3	11	66	23	4.33	1.3
4	20	60	20	9.80	0.9
5	30	52	18	12.90	1.6

When the weight percent of SAMMS was kept relatively constant at 10% and the weight percent of oil was increased from 23% to 30%, the voltammetric responses decreased. As the fraction of oil increased, the electrode surface had increasing hydrophobicity and hence a decrease in the surface reaction between the metal ions and the functional ligands.²⁷ When the oil content was kept relatively constant at nominally 20 wt. %, increasing the weight percent of SH-SAMMS from 11% to 30% increased the voltammetric responses due to the increase in number of the

binding sites. However, the reliability of the 30% SH-SAMMS electrode was poor after only 10 consecutive runs, whereas the reliability of the 20% SH-SAMMS electrode was still good even after 80 consecutive runs. When the composition of the electrode matrix included too high of a SH-SAMMS loading and too low of an oil loading, the electrode had poor reproducibility because the electrode material was not compact enough.²⁷ Therefore, the optimum electrode composition was 20% SAMMS, 60% CPO carbon paste, and 20% mineral oil (electrode #4).

4.2.3 Calibration and detection limits

The calibration curve represents the voltammetric response (current and area) versus the metal ion concentration in the preconcentration solution. The experiments were performed on the optimal electrode and conditions found in previous sections (electrode #4: 20% SH-SAMMS, 60% CPO carbon paste, and 20% oil; conditions: 60 seconds electrolysis time, and 0.2 M HNO₃ as the electrolysis and stripping media). Figure 7 shows representative voltammograms: (a) measured after 2 minutes preconcentration in a 30 ppb Pb²⁺/160 ppb Hg²⁺ solution, and (b) measured after 20 minutes preconcentration in a 1.5 ppb Pb²⁺/3 ppb Hg²⁺ solution. Figure 7 also shows that Pb²⁺ and Hg²⁺ peaks appear at -0.5 V and 0.4 V, respectively. The differential potential (ΔE) of 0.9 V indicates that the Pb²⁺ and Hg²⁺ peaks are not likely to interfere with each other, and hence the metals could be detected simultaneously.

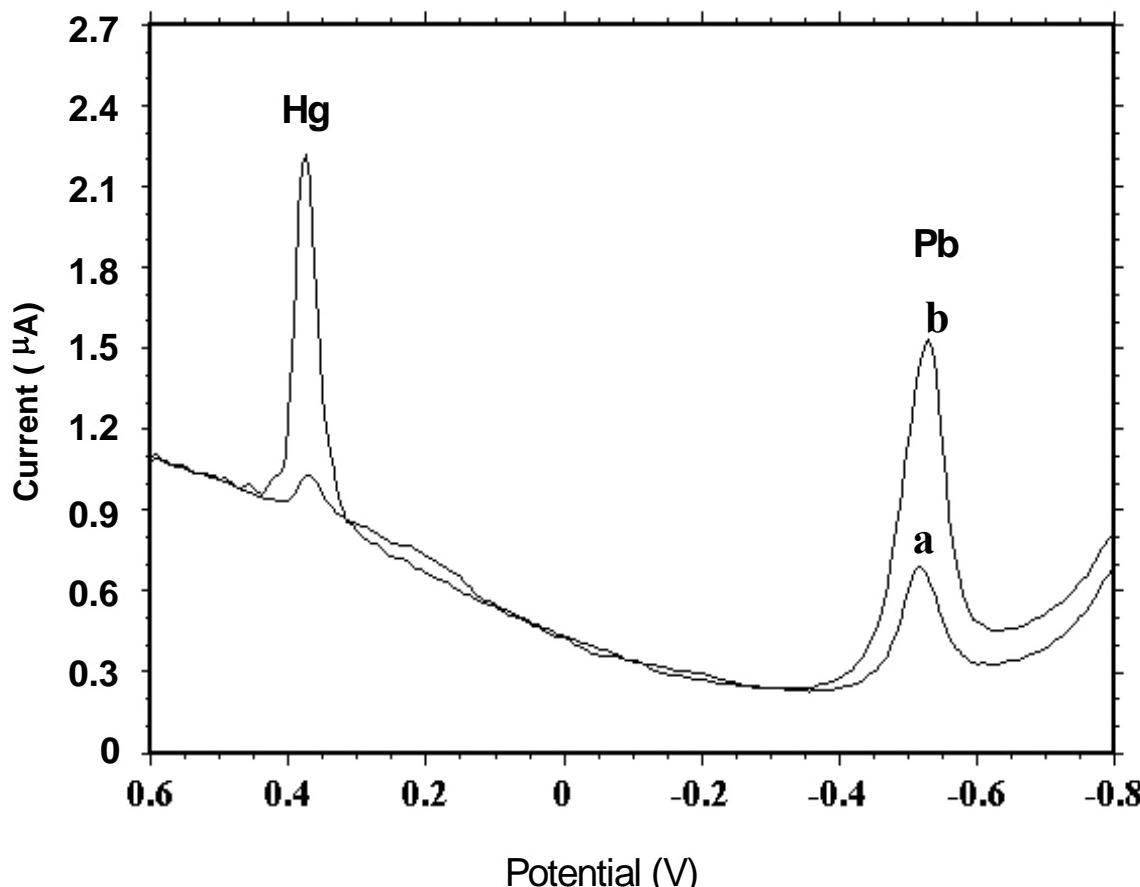


Figure 7: Voltammetric response after (a) 2 minute preconcentration in 30 ppb. Pb²⁺/160 ppb. Hg²⁺, and (b) 20 minute preconcentration in 1.5 ppb. Pb²⁺/3 ppb. Hg²⁺

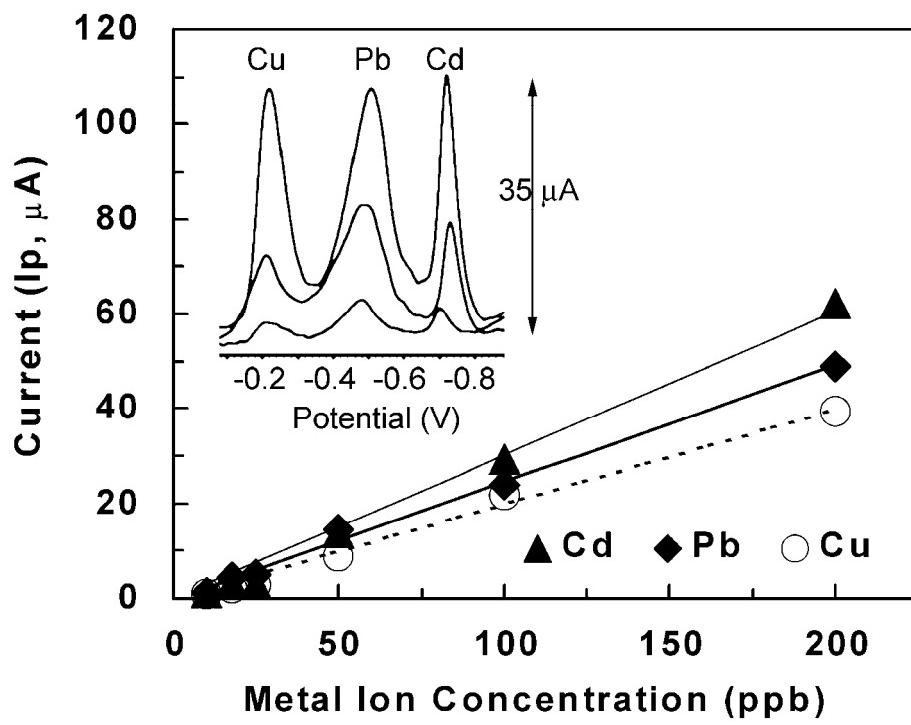


Figure 8a: Calibration curves for metal ion detection; current vs. concentration

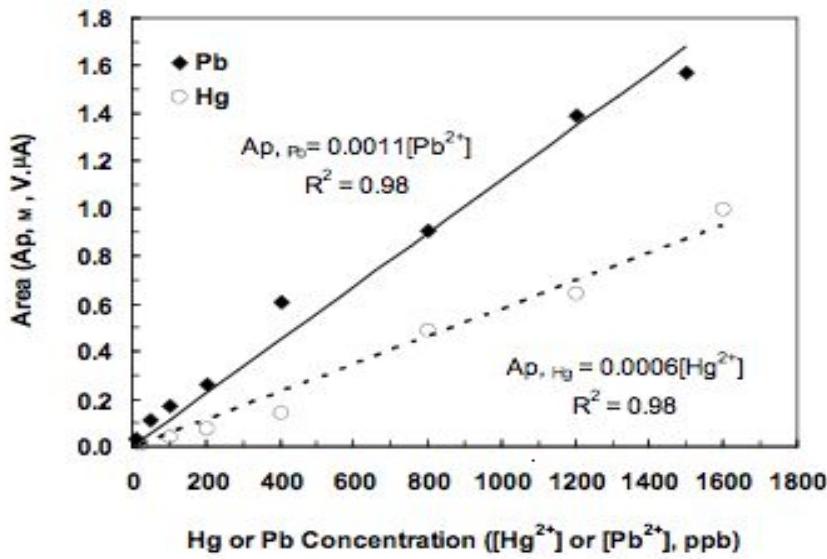


Figure 8b: Calibration curve for Pb and Hg response: peak area vs. concentration.

Figure 8 shows the calibration curves as (a) currents and (b) areas of the Cd, Pb and Hg peak responses, measured after 2 minutes preconcentration time in a tri-component Cd²⁺/Pb²⁺/Hg²⁺ solution. For each of the metal ions, the peak area appeared to be more useful as the detection response because it was linear with respect to metal ion concentrations for broader ranges than the peak current.

When varying the concentration ratios of Hg²⁺ and Pb²⁺ in the preconcentration solution from 0.5 to 2.0, the peak responses obtained for the two metal ions were still on the calibration curves. Therefore, the peak response for Hg²⁺ was independent of the concentration of Pb²⁺ in the solution and vice versa. Two factors may have contributed to this behavior: (1) the concentrations of both metal ions in solution were well below saturation point, thus metal ions did not need to compete for the binding sites, and (2) the pore size of the SH-SAMMS was large enough that the diffusion of the two metal ions was not limited by their hydrated sizes. This is a major advantage of SAMMS modified carbon paste electrodes compared with SAM thin film electrodes and organic ligand modified carbon paste electrodes.

Detection limits were evaluated at the same conditions as in the calibration curve measurements. The detection limit for Pb²⁺ was 10 ppb after a 2-minute preconcentration period and improved significantly to 0.5 ppb after a 20-minute preconcentration period. Similarly, the detection limit for Hg²⁺ was 20 ppb after a 2-minute preconcentration period and improved to 3 ppb after a 20-minute preconcentration period.

4.2.4 Electrode activation and regeneration

A virgin electrode surface was found to be less efficient (i.e., low peak response and low reproducibility) for preconcentration than surfaces that had previously been exposed to metal ions. For example, the voltammetric responses of 100 ppb Pb²⁺ at the electrode #3 (Table 4) stabilized after 3-4 cycles of preconcentration/electrolysis/stripping. To avoid a time-dependent

sensitivity in subsequent runs, all freshly made electrodes were activated by going through five cycles of preconcentration/electrolysis/stripping.

The extent of electrode regeneration depended on the concentration of the stripping acid and the size of the peak responses, which in turn were proportional to the amount of metal ion accumulated on the surface. When stripping in 0.2 M HNO₃ solution and the peak current was smaller than 5 μ A, regeneration of the electrode was not required (no metal ion peak detected after the re-sweep), which differed from the results when stripping in 0.05 M or 0.1 M HNO₃. A higher acid concentration was better for desorption of lead and preventing the desorbed species from being re-accumulated on the surface than the lower acid concentration. For example, the re-sweep after the detection of 100 ppb Pb²⁺ at electrode #3 (approximate current of 4 μ A) yielded a residual peak current of 1.0 μ A, 0.2 μ A, and 0.0 μ A when 0.05 M HNO₃, 0.1 M HNO₃, and 0.2 M HNO₃ were used as the electrolysis/stripping media, respectively. The larger the peak response was, the longer the period that was required for regeneration. However, regeneration in 0.2 M HNO₃ solution was normally accomplished within 1-2 minutes for a peak current size of 5-20 μ A.

4.2.5 Interferences

An ionic species may be considered as an interference to the voltammetric detection of mercury(II) and lead(II) if: (1) it can out-compete Hg and Pb for the binding sites on SH-SAMMS during the preconcentration step, or (2) its peak response can overlap Hg or Pb peak in the detection step. The first factor may be indicated by the selectivity of the SH-SAMMS material for that ionic species, compared with those for Hg and Pb. From batch competitive adsorption experiments previously performed at PNNL¹², we have learned that the SH-SAMMS sorbent has exceptional affinity for binding Hg and Pb. For example, in the presences of Ag, Cr, Zn, Ba, and Na, the SH-SAMMS sorbent has demonstrated the mass-weighted distribution coefficients (K_d) of Hg and Pb on the order of magnitude of 10⁵ at neutral pH. The high K_d values are a result of thiol being a “soft” ligand, which preferably binds with “soft” Lewis acids like Hg and Pb. The background ions, such as sodium, barium, and zinc, although present at high concentrations (i.e., 350 times higher concentrations than Hg and Pb) did not bind to the SH-SAMMS. Other “soft” Lewis acids like Cd, Cu, Ag, and Au, may also bind to the SH-SAMMS, but not as effectively as Hg and Pb. The K_d values of Cu and Cd, for instance, are about twenty-five times lower than those of Hg. In addition, the redox potentials of these metal ions (Cd, Cu, Ag, and Au) are different from those of Hg and Pb, thus their peak responses will not overlap with those of Hg and Pb. The presences of anions (i.e., CN⁻, CO₃²⁻, SO₄²⁻, PO₄³⁻) which might be expected to compete with the SAMMS capture ligands also did not significantly interfere with the adsorption of lead and mercury ions onto the SH-SAMMS and are thus presumed to not be likely to interfere with the detection of lead and mercury.

5.0 CONCLUSIONS

The SH-SAMMS modified carbon paste electrode coupled with an anodic stripping voltammetry technique can be used to detect lead (II) and mercury (II) simultaneously. The SH-SAMMS modified carbon paste electrode has many advantages over the existing chemically modified electrodes (CMEs), which normally use commercially-available ligands as the modifiers. The high surface area of the mesoporous silica and the covalent binding between the thiol (-SH) groups in SH-SAMMS and metal ions in solution make SAMMS a better sorbent than existing commercial ligands.¹⁰ The SH-SAMMS has been shown to be dramatically faster and more selective for adsorption of Hg, with the selectivity a factor of 1000 higher than that of DuoliterTM GT-73¹⁰, an organic ion exchange resin commonly used for Hg removal. The selectivity of SH-SAMMS to the target metal ions (Hg and Pb) is excellent. SAMMS will not accumulate common metal ions such as sodium and calcium, which are often present in wastewaters at much higher concentrations than the target ions. The high loading capacity and high selectivity of SH-SAMMS are desirable for metal ion detection based on the AdSV technique because they minimize the competition for the binding sites of the non-target species, thereby reducing the interferences and preserving the signal intensity of the target metal ions. Besides, since SAMMS particles are not conductive, the high surface of the material does not contribute to the charging current of the SAMMS modified carbon paste electrode. This leads to the low background current of the electrode. The binding between SH-SAMMS and metal ions is reversible, therefore the SH-SAMMS based electrodes can be easily regenerated without damaging the ligand monolayer by desorption of the preconcentrated species in an acidic solution. By choosing an appropriate acid solution as a stripping medium, the electrodes usually are ready for reuse after the stripping voltammetric measurement. The special advantage of using SAMMS over other organic ligands is that de-aeration of the sample, electrolysis medium, and stripping medium is not required, making the SAMMS-modified electrodes suitable for integration into portable sensor devices for on-site metal detection. In addition, self-assembled monolayer chemistry readily allows installation of a wide variety of chemical monolayers that can be tailored to specific metal ion detection needs when used as electrode modifiers.

APPENDIX: PRESENTATIONS & PUBLICATIONS

Presentations:

1. Y. Lin "Microfluidics/Nanoengineered Electrochemical Sensors for Environmental and Health Monitoring." Invited. BioMEMS 2003, June, San Jose, CA
2. Y. Lin "Electrochemical sensors based on Nanomaterials." Invited Keynote Lecture at Asianalysis VII, Hong Kong, August, 2003

Publications:

1. G. E. Fryxell, R. Shane Addleman, S. V. Mattigod, Y. Lin, T. S. Zemanian, H. Wu, Jerome C. Birnbaum "Self-Assembled Monolayers on Mesoporous Supports (SAMMS): Environmental Clean-up and Enhanced Sensing Capability." Invited article for *Encyclopedia of Nanoscience and Nanotechnology*, ed. J.A. Schwartz, C. Contescu, K. Putye, pp. 1125-1135; Marcel Dekker Inc. New York (2004)
2. Yantasee, W.; Lin, Y.; Fryxell, G.E.; Busche, B.J.; Birnbaum, J.C. "Removal of heavy metals from aqueous solution using novel nanoengineered sorbents: self-assembled carbamoylphosphonic acids on mesoporous silica." *Sep. Sci. Technol.*, accepted.
3. Yantasee, W.; Lin, Y., Zemanian, T.S., Fryxell, G.E. "Voltammetric detection of lead (II) and mercury (II) using a carbon paste electrode modified with thiol self-assembled monolayer on mesoporous silica (SAMMS)." *Analyst* **128(5)**, 467-472 (2003)
4. Yantasee, W.; Lin, Y.; Fryxell, G.E.; Busche, B.J. "Simultaneous detection of cadmium(II), copper(II), and lead(II) using a carbon paste electrode modified with carbamoylphosphonic acid self-assembled monolayer on mesoporous silica (SAMMS)." *Anal. Chim. Acta.*, submitted.
5. Yantasee, W.; Lin, Y.; Li, X, Fryxell, G.E.; T.S. Zemanian. "Nanoengineered Electrochemical Sensor Based on Mesoporous Silica Thin-film Functionalized with Thiol Monolayer." *Analyst* **128(7)**, 899-904 (2003)
6. Yantasee, W.; Lin, Y.; Alford, K.L.; Busche, B.J.; Fryxell, G.E.; Engelhard M. "Electrophilic aromatic substitutions of amine and sulfonate onto fine-grained activated carbon for aqueous-phase metal ion removal." *Envi. Sci. Technol.*, submitted.
7. Yantasee, W.; Lin, Y.; Alford, K.L.; Busche, B.J.; Fryxell, G.E.; Johnson C.D. "Selective removal of copper(II) from aqueous solutions using fine-grained activated carbon functionalized with amine." *Ind. Eng. Chem. Res.*, submitted.

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